Characterization of Low-Rank Coal Char
Used in the Production of Hydrogen

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INTRODUCTION

The production of low-cost hydrogen for use as a fuel and chemical feedstock to supplement fossil fuels and provide a feasible alternative to current hydrogen production methods is of continued interest in the energy field. The demand for hydrogen is increasing, with the need for hydrogen predicted to rise by a factor of 15 to 20 times over the next 40+ years (1).

Presently industrial quantities of hydrogen are produced primarily by either steam reforming of natural gas or partial oxidation of petroleum. However, both of the feedstocks for these processes are used more efficiently and economically in their chemically unaltered or physically refined forms. One of the most viable alternatives for hydrogen production, in terms of available feedstock, is in the use of advanced coal gasification processes. In coal gasification processes, hydrogen is produced by the following reactions:

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) \qquad 1)$$
$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g) \qquad 2)$$
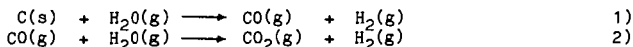
The gasification reaction 1) involves reacting coal char and steam to produce carbon monoxide and hydrogen. Additional hydrogen is produced via the water/gas shift reaction 2). The gasification step, reaction 1), is enhanced at reaction temperature by the presence of catalysts, of which the most widely studied are alkali salts (2). The alkali carbonates, bicarbonates, oxides, and hydroxides are well known as rate enhancers, while halides of the alkalis do not function nearly as well as positive catalysts. Low-rank coal offers a plentiful and relatively inexpensive substrate from which to form char that has high reactivity (higher than those of higher-rank coals) toward steam in a char-steam reaction 1) to produce hydrogen.

The thermodynamics of the water/gas shift reaction 2) require that the hydrogen production process operate at the lowest temperature possible. The limit to which the temperature may be lowered in the process is governed by the activity of the char generated at that temperature from a particular coal. Laboratory-scale experiments have shown that the 700°-800°C range at ambient pressure provide conditions for maximum production of hydrogen in the gaseous product (3). The catalytic enhancement of the rate of hydrogen production allows the operating temperature to be lowered, thus effecting greater shift and maximizing hydrogen formation.

Potassium carbonate is probably the most extensively studied of the alkali salt catalysts and is often used as a standard for comparison of catalyst effects. Other potassium compounds (except for the halides) have been shown to be excellent catalysts for the gasification of coal chars (4,5). Sodium compounds have also been studied extensively for their effect on the gasification reaction. They too have been shown to be good catalysts and in some cases were as good as the potassium compounds (5). Trona and nahcolite, naturally occuring sodium-rich minerals, have been shown in laboratory-scale experiments to be as good as potassium carbonate for catalyzing the char-steam reaction of some low-rank coals (5).

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From an economic standpoint, the sodium compounds are less expensive than potassium compounds, and mineable sodium-rich minerals are even less expensive than the pure sodium compounds. However, not all low-rank coals give the same reactivity or realize the same catalytic rate enhancement under the same reaction conditions; i.e., coal-specific effects are often evident. Therefore, thorough characterization of the chars generated at the various temperatures of interest and their response to various catalysts are important in understanding the mechanism of the gasification reaction in the production of hydrogen. The research reported here involves the characterization of chars from two low-rank raw coals, Velva (North Dakota) lignite and Martin Lake (Texas) lignite. The chars were generated in the temperature range 650°-750 °C, at atmospheric pressure under inert atmosphere. Chars were also prepared from Velva and Martin Lake lignites containing added catalyst (10 wt% K_2CO_3 and Trona) at the same conditions for characterization.

EXPERIMENTAL

The reaction between low-rank coal chars and steam to produce hydrogen was studied with two different Thermogravimetric Analysis (TGA) systems. The kinetic study of weight change of carbon with time for the char-steam reaction was carried out on a DuPont 951 Thermogravimetric Analyzer (TGA) interfaced with a DuPont 1090 ThermalAnalyzer. Approximately 20 mg samples of -100 x +140 mesh uncatalyzed or catalyzed coal were devolatized under argon flowing at 160 cc/min, and the resulting char was reacted with steam ($p_{(H_2O)}$ = 0.1). Weight, time, and temperature data were recorded, and each experiment was terminated when weight loss ceased. Total gas (product gas plus carrier gas) samples were collected over the duration of the run and were analyzed by gas chromatography (GC). Selected experiments were duplicated on a large TGA so that larger gas samples could be collected, ensuring sufficiently accurate analysis. The large TGA was built at the University of North Dakota Energy Research Center (UNDERC) using a Cahn 1000 electrobalance and a 1200°C vertical tube furnace for reacting samples >1 g. Reactivity parameters, (k), for 50% carbon conversion, were calculated at each of three temperatures (T) and Arrhenius plots of ln k vs 1/T were constructed for calculating energy of activation (Ea) and frequency factor, (A), as previously described (3). Residue remaining after the reaction was analyzed by X-Ray Diffraction and X-Ray Fluorescence techniques.

Char analyzed by spectroscopic techniques was prepared as in the char-steam reaction experiments, but was cooled to room temperature under argon. In selected experiments the char was removed from the TGA under argon and stored under argon to prevent exposure to air. These samples were analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) and solid state [13]C Cross Polarization/Magic Angle Spinning (CP/MAS) Nuclear Magnetic Resonance Spectrometry (NMR). Catalyzed and uncatalyzed samples of char were examined by Scanning Electron Microscopy (SEM), to determine surface elemental composition and to obtain photographs of the char surface. The field was scanned and representative particles were photographed and mapped to determine elemental distribution. All char samples were analyzed for active sites by gravimetric measurement of CO_2 adsorption in a manner similar to that described by Ratcliffe and Vaughn (6).

RESULTS AND DISCUSSION

There are several significant chemical differences between the coals used in this study. The Velva lignite is a northern Great Plains lignite, whereas the Martin Lake lignite is a Gulf Coast lignite and as such reflect significantly different coal-forming environments. Proximate and ultimate analyses of the two coals are listed in Table 1. The Martin Lake sample was higher in moisture and significantly lower in ash content than the Velva sample. The moisture-free (mf) oxygen value for the Martin Lake coal is 18% lower than that for the Velva, and the C/H ratio is 1.18 for Martin Lake compared to 1.30 for Velva. The normalized

product gas compositions shown in Table 2 were determined by gas chromatography (GC) on the total gas sample collected during the hydrogen production reaction carried out on both the DuPont TGA and the large laboratory TGA. The normalized hydrogen values approximated those predicted by the engineering thermodynamic model. The values obtained from the samples generated on the large TGA have somewhat less uncertainty in analysis since the dilution effect of the carrier gas was reduced.

TABLE 1

PROXIMATE AND ULTIMATE ANALYSES

Proximate Analyses	Velva	Martin Lake
Moisture %	29.3	34.8
Ash, wt % mf	13.5	8.7
Volatile Matter, wt % mf	39.3	44.0
Fixed Carbon, wt % mf	47.2	47.4
Heating Value, Btu/lb	7185	7525
Ultimate Analyses, mf		
Hydrogen	3.84	4.71
Carbon	59.93	66.46
Nitrogen	0.94	1.18
Sulfur	0.53	0.86
Oxygen (Diff)	21.26	18.09

TABLE 2

PRODUCT GAS IN MOLE % FROM VELVA LIGNITE CHAR-STEAM REACTION - LARGE TGA

Sample*	Temp. °C	H_2	CO_2	CO	CH_4
W/10 wt% Trona	750	56.23	30.13	13.64	ND
W/10 wt% Trona	700	51.73	43.51	4.55	ND
Uncatalyzed	750	57.70	35.30	6.30	0.72
Uncatalyzed	700	56.20	40.00	2.60	0.90

ND = Absent or below detection limit

*Sample sizes were between 1.0 and 1.4 grams of -100 +140 mesh "as received" coal- catalyst.

Data normalized to exclude carrier gas and air.

The inherent mineral matter of the Velva lignite had the effect of increasing the reaction rate over that of the Martin Lake lignite. Addition of either potassium or sodium compounds also increased the rate of the char-steam reaction for both the Martin Lake and the Velva char. Potassium carbonate and Trona admixed with the lignite both gave positive catalysis of the char-steam reaction. The activity parameter (k in g/hr/g) increased from 1.40 with no catalyst to 3.50 with 10 wt% K_2CO_3 and to 3.23 with 10 wt% Trona for Velva lignite at 700^oC. The reactivity parameter also increased from 0.74 with no catalyst addition to 1.41 with 10 wt% K_2CO_3 and 2.37 with 10 wt% Trona for Martin Lake lignite at 700^oC.

SEM photographs (Figure 1) show the surface effect, upon charring, of adding K_2CO_3 catalyst to the coals. The ragged, irregular surface and lack of apparent pores in the uncatalyzed char is in contrast to the rounded, highly porous surface on the alkali catalyzed char. The degree to which the surface changed with the addition of catalyst differed between the Velva and the Martin Lake chars. The Velva char surface is remarkably porous and contained uniform, evenly spaced nodules of approximately 0.05 μm x 0.10 μm in size. The nodules on the surface of the catalyzed Martin Lake char were neither uniform in size nor evenly spaced over the surface. The reactivities differed similarly, with the Velva having the higher reactivity. This suggests that the increase in reactivity of the catalyzed char, which may be due to mechanistic change in the chemical reaction brought about by the alkali catalyst, must also be due, at least in part, to the physical effect of producing a large increase in surface area. The result of this increase in surface area is an increase in available active sites as shown in Figures 2 and 3 for Velva char and Martin Lake char, respectively.

SEM mapping of the surface for inorganic element distribution showed that the potassium was distributed uniformly over the surface of the Velva particles. This was not the case with the Martin Lake particles. The uniform distribution of the potassium catalyst on the surface of the Velva char implies a surface wetting by a fluid consisting of, or containing, the catalyst. The Trona, however, does not exhibit this mode of distribution. Instead the element distribution map showed the sodium surface deposits as being associated with those of silicon and aluminum. The irregularly placed surface nodules of nonuniform size were located near the sodium deposits.

Carbon 13 Nuclear Magnetic Resonance (^{13}C NMR) spectra of chars prepared at temperatures from 600° to 750^oC (Figure 5) indicated the absence of aliphatic groups in the char with removal of aliphatics occurring during the charring process. Aromatic CO groups and carboxyl, amide, and ester groups are absent in the chars as well. The decrease in aromatic signal strength with temperature may result from unobserved carbon in CP/MAS due to the decrease in H/C with the char (7). Table 3 shows the ESCA surface carbon/oxygen ratio on the Velva chars prepared at various temperatures. Char prepared at 750^oC and exposed to air had a significantly lower surface C/O ratio than that prepared at the same temperature and protected from exposure to air. The latter sample was analyzed at the natural surface, and then at surfaces produced by removal of outer layers of char using ion "sputtering" for the time indicated on Table 3. The low C/O ratio of the exposed sample is due to the adsorption of oxygen on exposure to air. Higher oxygen contents are related to the highly activated carbon that results during the char formation. The chars formed at the other temperatures given on Table 3 exhibited little increase in C/O ratio with temperature. These results indicate that erroneous surface data can be minimized by maintaining an inert atmosphere over the char samples and a more accurate analysis can be carried out.

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TABLE 3

ESCA RESULTS--VELVA LIGNITE CHAR (ELEMENT %)

Char Temp. (°C)	Sputter Time (minutes)	Element %			
		C	O	N	C/O
750*	0	74.4	21.0	---	4.73
750	0	82.1	14.3	---	7.69
	10	82.9	13.0	---	8.52
	70	84.3	11.6	---	9.62
700	70	81.9	10.9	0.9	10.03
650	70	80.1	12.3	0.8	8.66
600	70	80.3	12.6	1.0	8.47

*Exposed to air

CONCLUSIONS

- Reactivity of low-rank coal chars are increased by factors of two to four at a given temperature with addition of catalyst.
- The increased reactivity is due to increases in surface area and active sites.
- Scanning electron microscopy shows that catalyzed chars have a much higher surface area than uncatalyzed chars.
- Potassium was distributed more uniformly than the trona over the char surface.
- The highly activated carbon created by the devolatilization of the low-rank coal necessitates the prevention of exposure to air if CO functional groups are to be accurately identified by ESCA or quantified by CP/MAS ^{13}C NMR.

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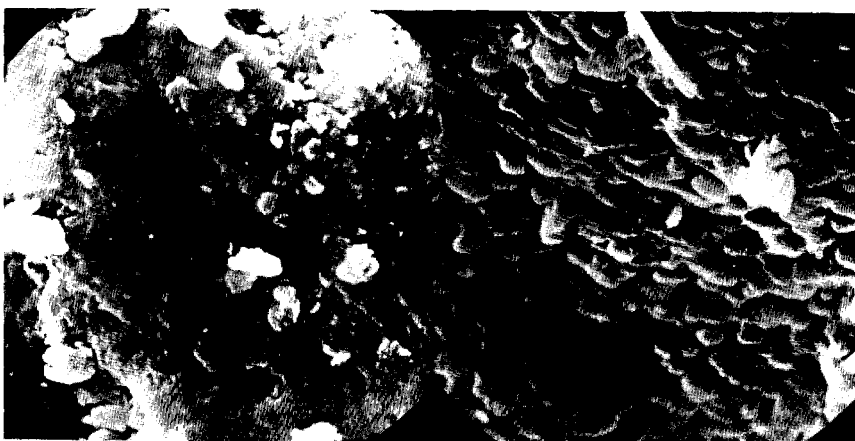## ACKNOWLEDGEMENTS

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a) Martin Lake Char - Mag. 6000X   b) Martin Lake/K_2CO_3

c) Velva Char - Mag. 6000X   d) Velva/M_2CO_3 Char - Mag. 6000X

Figure 1 - SEM Photographs of Coal Chars and
Coal/K_2CO_3 Char Prepared at 750°C
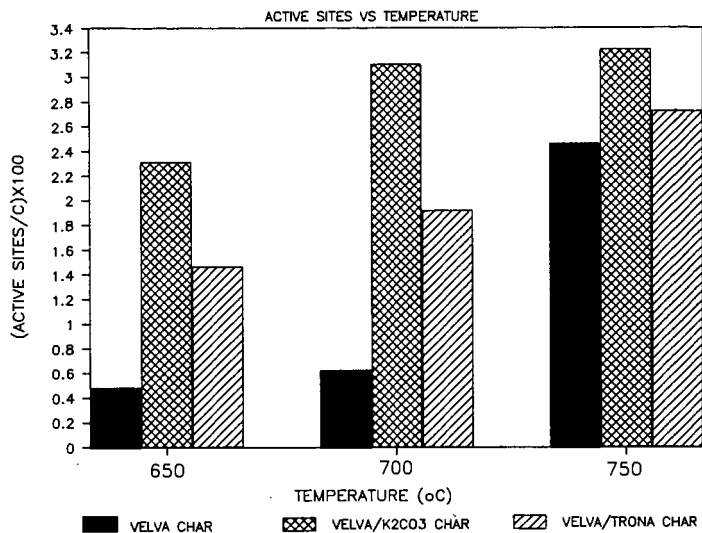
UNCATALYZED AND CATALYZED VELVA CHARS

ACTIVE SITES VS TEMPERATURE

Figure 2. Number of active sites/carbon atom in Velva lignite char with and without catalyst.
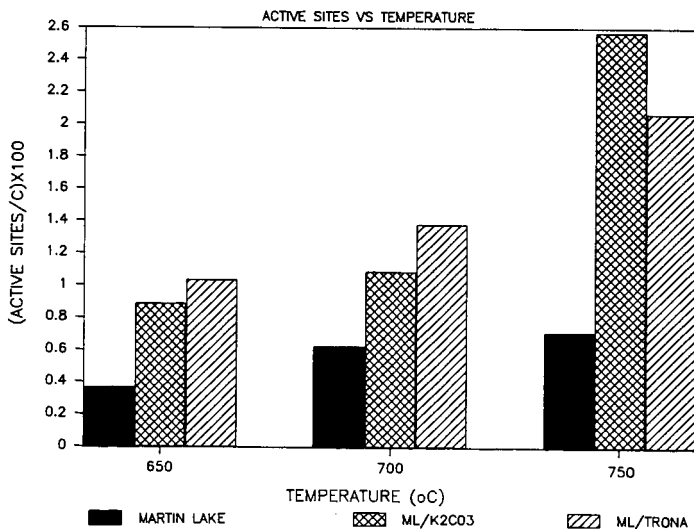
MARTIN LAKE CHAR

ACTIVE SITES VS TEMPERATURE

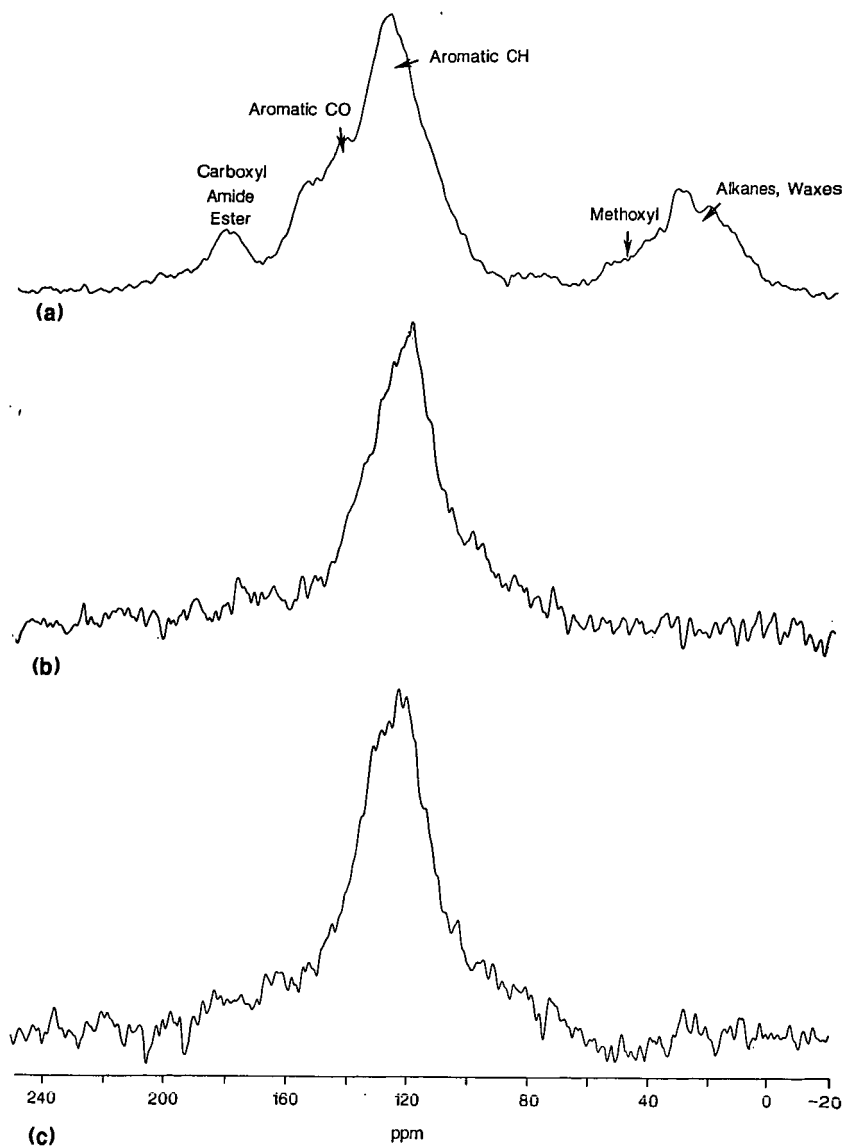Figure 3. Number of active sites/carbon atom in Martin Lake lignite char with and without catalyst.

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Figure 4. CP/MAS ^{13}C NMR Spectra of (a) Velva North Dakota lignite (b) Velva lignite char (750^oC) and (c) Velva/Trona char 750^oC.
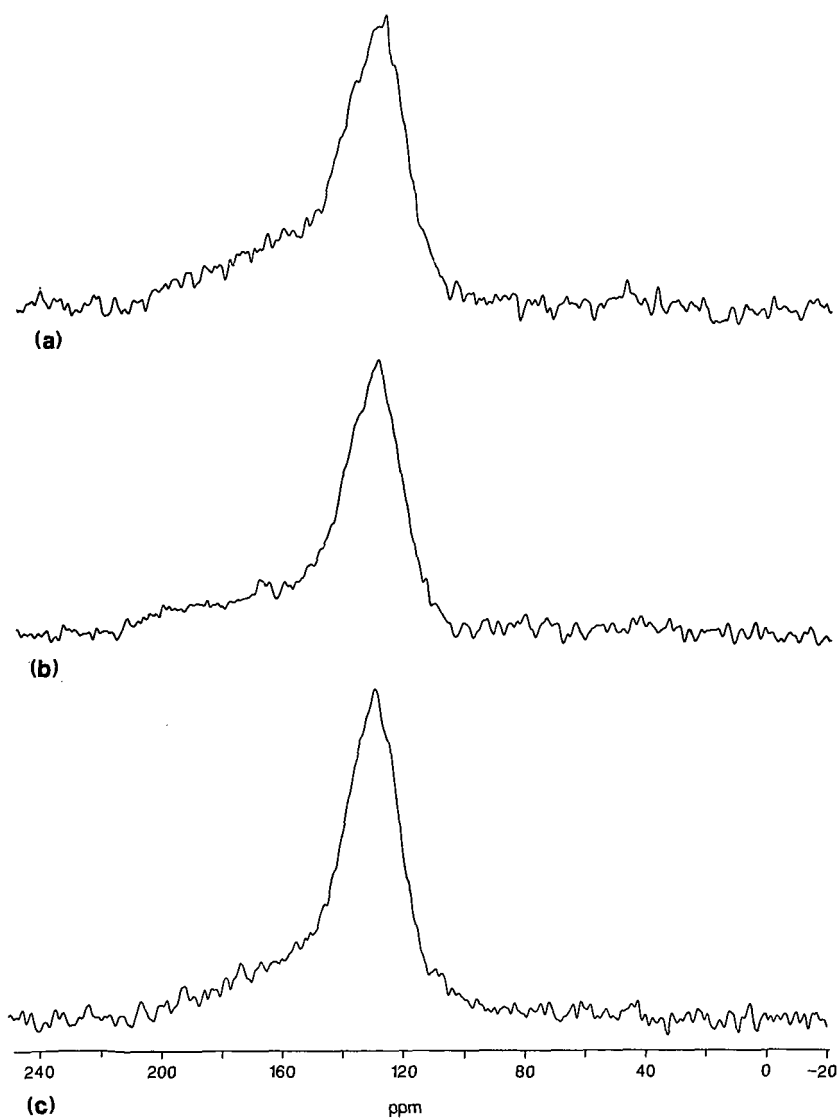
Figure 5. CP/MAS ^{13}C NMR spectra of Velva/Trona char prepared at (a) 700°C (b) 650°C, and (c) 600°C.